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COLLOÏDES RICHES EN MATIÈRES ORGANIQUES ET EN FER DANS TROIS DES PRINCIPALES RIVIÈRES DU BASSIN VERSANT DE L'ARCTIQUE EN ONTARIO

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ORGANIC AND IRON-RICH COLLOIDS IN THREE MAJOR RIVERS OF ONTARIO'S ARCTIC WATERSHED

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ABSTRACT

Water samples from three northern Ontario rivers (Winisk, Attawapiskat, Moose), known to have elevated levels of naturally-occurring organic matter, were sampled in 1984-1985. These samples were fractionated by means of filtration (0.65 μm pore diameter) followed by an ultracentrifugation step (105,000 g) to divide the aqueous (or "non-particulate") fraction into dissolved and colloidal fractions. The fractions were analyzed for organic carbon and iron content, and they were examined by transmission electron microscopy and energy-dispersive spectroscopy. The colloidal fraction was characterized in terms of the structure, size, shape and relative iron level of the major colloidal "particulates". One colloid, a metal-rich spheroid (0.015-0.060 μm diameter), was dominant in all colloidal fractions. Other major colloid types were fibrils (0.003-0.020 μm diameter) and spherules (0.003 μm). In most colloidal fractions, there were no iron-rich particulates in the upper size range for colloids (0.1-1.0 μm least diameter), with >95% of the total colloidal material having least diameters below 0.060 μm. Overall, the colloidal fraction accounted for 3.6% of conventionally-defined dissolved organic carbon, yet contained 40% of the iron of the aqueous fraction.

RÉSUMÉ

En 1984-1985, des échantillons d'eau furent prélevés dans trois rivières du Nord de l'Ontario - la Winisk, l'Attawapiskat et la Moose - dont la forte teneur en matières organiques d'origine naturelle était connue. Ces échantillons ont été fractionnés par filtration (filtre à pores de 0,65 µm), puis par ultracentrifugation (105 000 g) de façon à séparer la fraction aqueuse (ou "non particulaire") en une fraction dissoute et une fraction colloïdale. Nous avons déterminé la teneur en carbone organique et en fer de ces fractions et nous les avons ensuite examinées par microscopie électronique à transmission et par spectroscopie à dispersion en énergie. Nous avons caractérisé la structure, les dimensions, la forme et la teneur relative en fer des principales "matières particulaires" colloïdales des fractions colloïdales. Dans chacune d'elles, un colloïde prédominait, soit un sphéroïde (diamètre de 0,015-0,060 µm) riche en métal. Les autres principaux types de colloïdes avaient la forme de fibrilles (diamètre de 0,003 - 0,020 µm) et de sphérules (0,003 µm). Dans la plupart des fractions colloïdales, il n'y avait aucune matière particulaire riche en fer dans les colloïdes de grande taille (diamètre minimum de 0,1 - 1,0 µm); en outre, plus de 95 % des matières colloïdales totales avaient un diamètre minimum inférieur à 0,060 µm. L'ensemble de la fraction colloïdale renfermait 3,6 % du carbone normalement dit carbone organique dissous, mais elle contenait 40 % du fer de la fraction aqueuse.

PERSPECTIVE GESTION

Colloïdes riches en matières organiques et en fer dans trois des principales rivières du bassin versant de l'Arctique en Ontario

par

Gary G. Leppard, Robert C. McCrea et Dina Urciuoli

La fraction colloïdale des eaux fluviales est habituellement négligée au cours des études de la dispersion des métaux; on a tendance à n'envisager l'action du carbone organique colloïdal comme agent de dispersion des métaux que sous son aspect théorique. Selon le présent rapport, la fraction colloïdale de trois rivières du Nord de l'Ontario renferme 40 % du fer normalement considéré en solution. La majorité de ce fer est associé à une petite portion des colloïdes organiques, en particulier à des sphéroïdes dont le diamètre est compris entre 0,015 µm et 0,060 µm. Ces sphéroïdes échappent à beaucoup des techniques utilisées par les limnologistes pour déceler les matières colloïdales qui pourraient permettre d'interpréter les données relatives à la dispersion des métaux. Notre présente description des fractions colloïdales de ces rivières est probablement la première étude à haute résolution (résolution de 0,003 µm) de la structure, des dimensions, de la forme et des teneurs relatives en fer des principaux colloïdes fluviatiles.

MANAGEMENT PERSPECTIVE ---

NWRI Contribution No. 86-136

Organic and iron-rich colloids in three major rivers of Ontario's Arctic watershed

by

Gary G. Leppard, Robert C. McCrea and Dina Urciuoli

The colloidal fraction of river waters is usually ignored in considerations of metal dispersion; and colloidal organic carbon as a metal-dispersing agent tends to be considered in theoretical terms only. This report shows that, for three northern Ontario rivers, a colloidal fraction accounts for 40% of the iron normally attributed to the dissolved phase. Much of this iron is associated with a small fraction of organic colloids, and particularly with spheroids whose diameter is in the range of 0.015-0.060 μm. Such spheroids go undetected by many techniques used by limnologists. The descriptions of the riverine colloidal fractions provided here are probably the first high resolution (0.003 μm resolution) studies available on the structure, size, shape and relative iron levels of dominant riverine colloids.

INTRODUCTION

The Hudson Bay Lowland is a vast coastal plain extending from the south and west shores of Hudson Bay and James Bay to the Canadian Shield (Fig. 1). This region is characterized by a sedimentary limestone and shale bedrock overlain with marine clay, and has been described as the largest continuous peatland expanse in the world (Sims et al., 1979). Virtually the entire Lowland area is poorly drained and features extensive bog and fen complexes. The Ontario portion (265,000 km^2) of this immense peat complex encompasses five major rivers: the Severn, Winisk, Attawapiskat, Albany and Moose. Owing to the seepage of aquatic organic matter from the surrounding wetlands, the major rivers are often highly colored. Each one threads through deltas and/or expands into broad shallow estuaries before discharging into Hudson Bay and James Bay (Hutton and Black, 1975).

As part of an environmental baseline assessment of the area, the Water Quality Branch, Ontario Region, has undertaken a study to establish baseline water quality conditions in the major rivers. Heavy metal analyses have indicated the presence of high levels of total iron in each river with mean concentrations ranging from 260 to 860 µg/L (McCrea and Fischer, 1986). Of the samples analyzed, 79% were above the Ontario Ministry of the Environment objective (of 300 µg/L of Fe) for the protection of aquatic life. To a large extent, the elevated iron concentrations are due to suspended sediments. Water quality investigations of the Moose River, conducted in 1977-78, revealed that a significant concentration of iron (200 µg/L) was present in the conventionally-defined dissolved fraction (McCrea and Merriman, 1981). The major inorganic species of iron in natural waters is ferric hydroxide; however, this substance has a very low solubility in the pH range of 5 to 8 (Wetzel, 1975) and thus there is an interest in understanding the basis for iron abundance in rivers of the Hudson Bay Lowland.

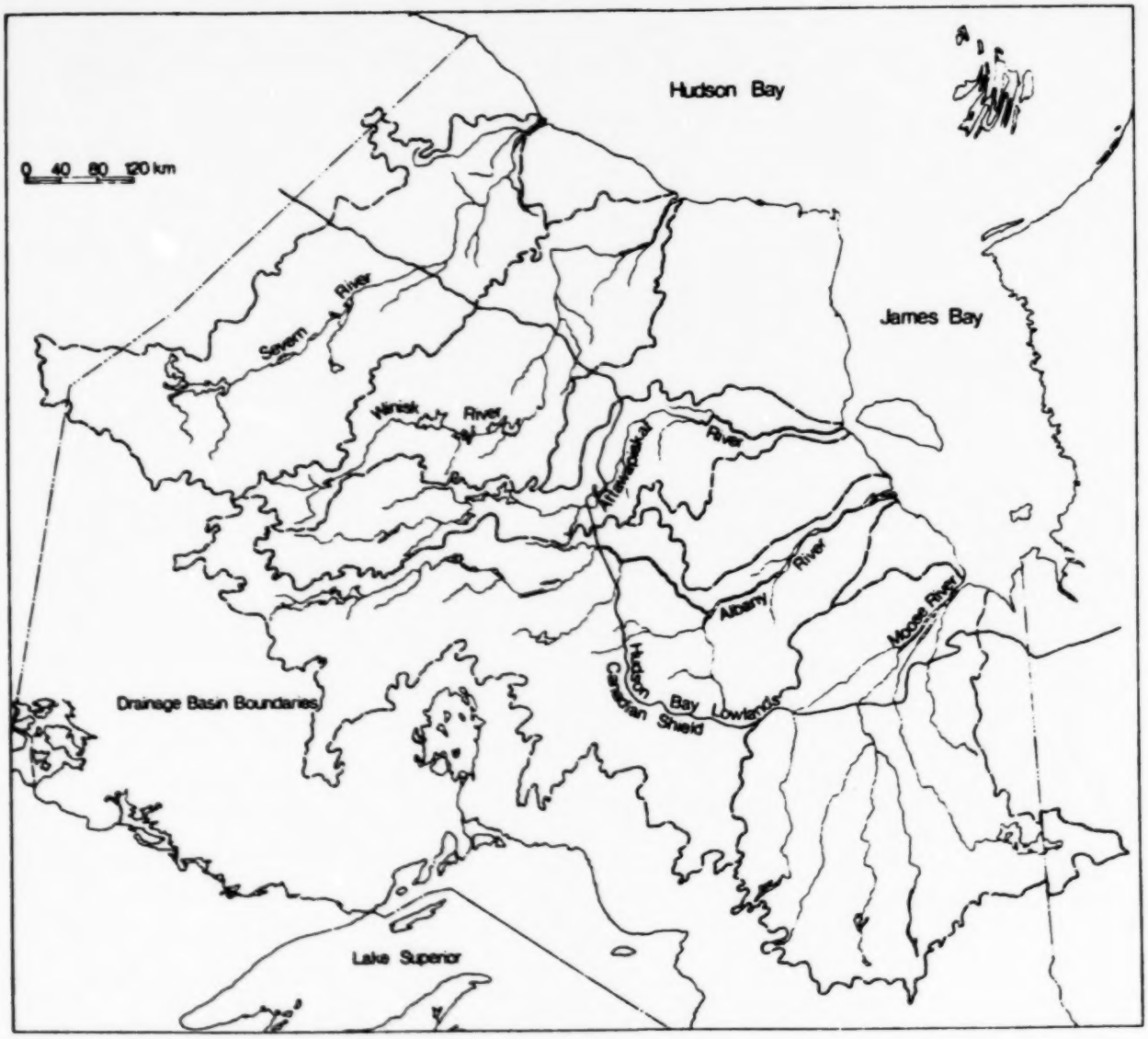


Fig. 1. Arctic drainage basins in Ontario.

In view of the elevated levels of both dissolved organic carbon (DOC) and iron in these northern Ontario rivers (McCrea, 1981; McCrea and Fischer, 1986), this study was undertaken to investigate the relationships between iron and DOC in the waters of the Winisk, Attawapiskat and Moose Rivers. An enrichment of iron in waters having a high organic content has been documented (Sholkovitz and Copeland, 1980; Kerndorff and Schnitzer, 1980; Mantoura, 1981; Schnitzer, 1981) and a focus is being placed on colloidal associations between iron and organic carbon (Florence and Batley, 1980; Leppard, 1984a). In this report, we consider: (1) the characterization of the major riverine colloid types; (2) the compartmentalization of iron within the two components of the aqueous fraction (the solute-rich dissolved fraction and the colloidal fraction); (3) the relative iron retention factor for the dissolved and colloidal fractions; (4) the pitfalls of considering conventionally-defined dissolved fractions, such as DOC, as consisting solely of water and solutes. For practical reasons, we have defined "colloid" according to the suggestion by Vold and Vold (1964); a colloid is any particulate having at least one dimension between 0.001 μm and 1.0 μm.

METHODS

Sampling

Raw water samples were collected seasonally in the fresh water regime of each river, 10 to 20 km upstream of their mouths and above possible contamination inputs from the nearby communities. During the open water season, samples were taken from midstream at a depth of 0.5 m using 2L polyethylene bottles. When a river was frozen over, a hole was drilled through the ice and, after the ice chips were removed, a sampling device was lowered into the free-flowing water for sample collection. All samples were shipped to the Canada Centre for Inland Waters (CCIW) in Burlington and subsequently stored at 4°C.

Fractionation and Chemistry of the Fractions

Fractionation of raw water samples was carried out as shown in Fig. 2, yielding suspended sediment, aqueous, dissolved and colloidal fractions for chemical, ultrastructural and energy-dispersive spectroscopical analyses. The suspended sediment fraction was collected on Whatman 0.65 µm glass fibre filters under an added pressure of 70 kPa. These filters were pre-ignited at 450°C for 2 hours and acid-washed to remove both organic and inorganic carbon. A portion of the filtrate, or "aqueous fraction", was centrifuged for 2 hours at 105,000 g and 5°C with an IEC B60 ultracentrifuge, yielding the "dissolved fraction" and the colloidal pellet. Twelve 30 ml centrifuge tubes were used for processing each sample. Pellets from ten of the tubes were resuspended in 300 ml of deionized/double-distilled water to provide the colloidal fraction. The remaining pellets were processed for ultrastructural analyses, including energy-dispersive spectroscopy.

The seston was analyzed for particulate organic carbon (POC) on a Hewlett-Packard CHN analyzer, whereas aliquots of the aqueous, dissolved and colloidal fractions were analyzed for DOC. All samples for DOC analysis were acidified with HNO_3 and heated to 120°C to release the inorganic carbon as CO_2. Then the organic carbon was converted to CO_2 in an ultraviolet digester and quantified with an infrared detector.

Aliquots of the raw water and of the water fractions were analyzed for total extractable iron. These subsamples were digested with HNO_3, buffered to pH 4.75 with a solution of ammonium pyrrolidine dithiocarbamate and extracted with methyl isobutyl ketone. The absorbance of the extract was measured on a Perkin-Elmer atomic absorption spectrophotometer and compared to standard solutions; subsamples above 50 ppb iron were measured by direct aspiration. All chemical analyses were performed by the Water Quality National Laboratory at the Canada Centre for Inland Waters in Burlington, Ontario.

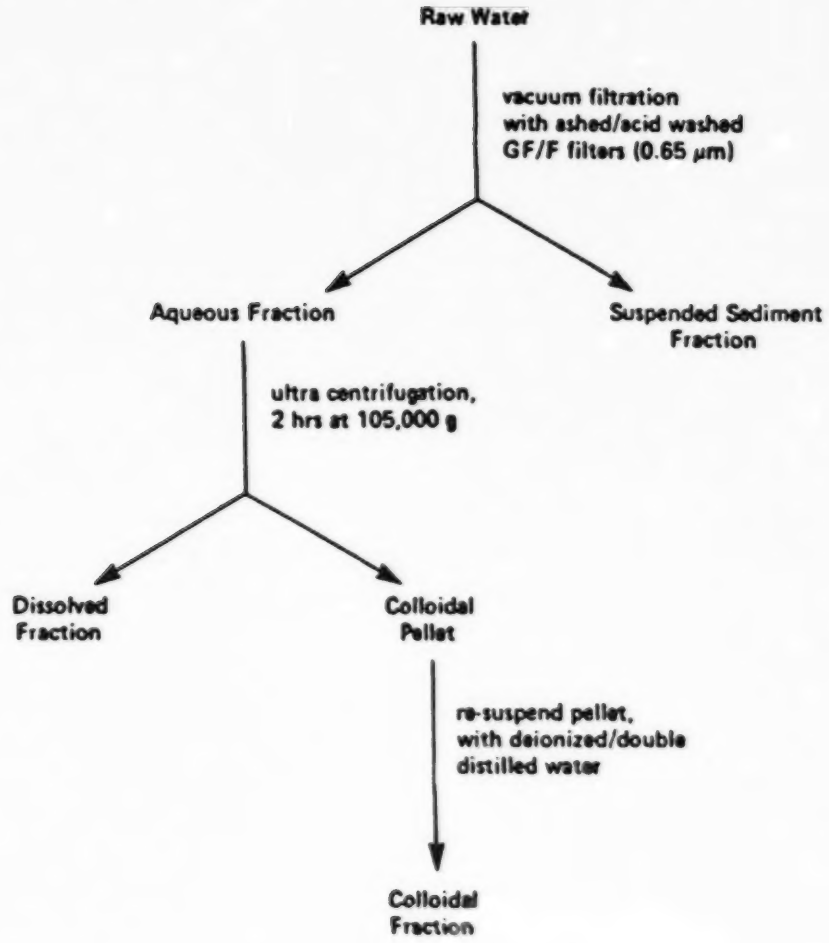


Fig. 2. The water fractionation scheme for deriving colloidal and dissolved fractions.

Conventional Transmission Electron Microscopy

All fractions and aliquots of raw water samples were prepared for ultrastructural analyses by the procedure of Burnison and Leppard (1983). The epoxy-embedded preparations (Spurr, 1969) were sectioned with a diamond knife mounted in an LKB ultramicrotome (Ultrotome III). The sections of 50-70 nm thickness, as estimated by the interference color method of Peachey (1958), were mounted on copper grids without a support film. After counterstaining, they were examined according to the systematic approach outlined in Leppard et al. (1977) with a Philips 300 TEM operated at an accelerating voltage of 60 kV. Counterstaining was done according to Leppard et al. (1986a); analysis of sections was confined to sections free of any counterstain precipitate.

The quality of the fractionation process was assessed as follows in a semi-quantitative manner according to Burnison and Leppard (1983). The raw water was compared with the suspended sediment and aqueous fractions; the aqueous fraction was compared with the dissolved and colloidal fractions. The analyses of the suspended sediment fraction were accomplished by sectioning the filter and its adhering particulates as a relatively undisturbed unit. This permitted an analysis of suspended sediments which encompassed particulates both within the filter pore structure and on the surfaces of the filter.

Energy-Dispersive Spectroscopy

A dual-stage scanning electron microscope (I.S.I. DS-130), equipped with a STEM attachment and an energy-dispersive X-ray analyzer (γ PGT-System 4), was used for energy-dispersive spectroscopic analyses (Chandler, 1977). An accelerating voltage of 15 kV was applied to 100-200 nm sections (derived as above for conventional TEM analyses) which were mounted on a carbon-coated,

formvar-covered, copper grid. The grid holder was tilted towards the detector from the horizontal at +10°, and 40 seconds was selected as the counting time. Only obvious peaks (peaks more than double the height of the background signal) were considered in assessing the relative amounts of iron per given sample volume and the relative concentration of iron in a given type of colloid (with this latter assessment based on colloid aggregates in the case of the smallest colloids).

An Assessment of the Heterogeneity of Iron Distribution within the Colloidal Pellet

Searches of colloidal pellets for contamination by iron-rich particles from the suspended sediment fraction (0.65 μm and greater in least diameter) were conducted as follows. Sections were selected at random and searched for 30 minutes by conventional TEM for particles of anomalously great size relative to the pore diameter of the cutoff filter. Using the assumption that some conventionally-defined particles could fragment during the fractionation process, sections were also searched for any distinctive particulates >0.1 μm whose morphological characteristics established them as possible fragments. Then the sections were searched again by STEM, with the search alternating between standard transmission images (to assess electron-opacity, a feature augmented by native iron) and X-ray dot maps for iron. The searches by STEM covered the colloidal range of particulates, but special attention was given to particulates in the range of overlap between small particles and large colloids (1.0-0.1 μm).

Whenever a "large" particulate was identified as electron-opaque by STEM, it was examined by energy-dispersive spectroscopy to compare its relative iron level to that of a nearby aggregate of small colloids having a similar diameter. In this way, thousands of individual colloidal particulates could be examined per section. Preliminary experimentation showed that the relative iron levels per

colloid type could not be ascertained in this manner for small colloids (3-60 nm least diameter = 0.003-0.060 μm least diameter); however, a densely packed aggregate sometimes yielded a well-defined peak.

As a check on the method of assessing the heterogeneity of iron distribution within a colloidal pellet, a water sample, known from a concurrent study on Severn River colloids to be exceptionally-rich in finely-dispersed iron, was processed exactly in the same manner as the major samples and examined by the same techniques and instruments. This sample (Severn River, spring, 1984) had a 1:5 ratio of colloidal iron: colloidal organic carbon and a 1:3 ratio of colloidal iron: suspended particulate iron. Unlike the samples from the three rivers of major interest, this Severn River sample contained many angular particulates in the 0.1 to 1.0 μm range.

RESULTS

Effectiveness of the Fractionation Procedure and Integrity of the Colloidal Fraction

Cross-contamination, as judged by high-resolution TEM, occurred at a low level similar to the best results found in the literature (Burnison and Leppard, 1983; Leppard et al., 1986a). As anticipated from these earlier works, the smallest colloids (as defined by Vold and Vold, 1964) in the colloidal fraction (as defined by the scheme of Fig. 2) and the largest colloids in the dissolved fraction formed a continuum; there is as yet no technically-feasible way (Leppard, 1985) to establish a distinctive cutoff between "dissolved" and "colloidal" materials, a problem which leads always to an underestimate of the colloidal fraction as defined by Vold and Vold (1964).

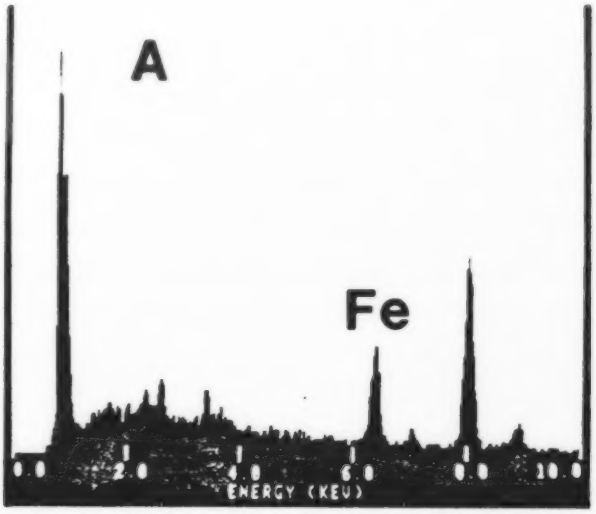
Special attention was devoted to assessing any contamination of the colloidal fraction by the suspended sediment fraction. From conventional high-resolution TEM (resolution of 2.5 nm), it was

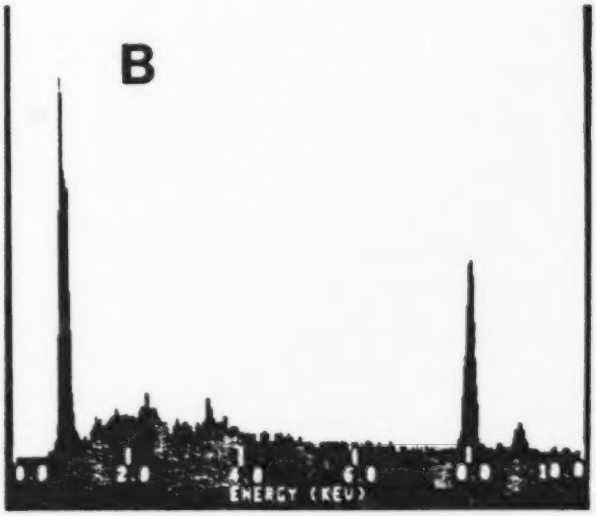
determined that no morphologically-distinctive type of fine particle (in the range of ca. 1/2 to 5 μm) was "partitioned" between the two fractions. From energy-dispersive spectroscopy, it was determined that both nondescript and distinctive particulates in the 0.10-0.65 μm range lacked iron measurable above the sensitivity limit (ca. 0.1% Fe within the irradiated volume of embedded colloidal material), with one exception (Fig. 3). Densely packed aggregates of colloids, individually smaller than 0.10 μm, gave a distinctive iron peak (Fig. 3A) when spheroids of 15-60 nm were present. The spring of 1984 sample from the Moose River was rich in such dense aggregates, which gave iron peaks of 3-8 times higher than baseline. Loose aggregates of small colloids, including electron-opaque colloids, and dense aggregates of the smallest colloids (3 nm electron-transparent spherules - see below) generally revealed no iron peak by energy-dispersive spectroscopy (Fig. 3B). In contrast to the three rivers of major interest, the Severn River sample was enriched in 0.10-0.65 μm particulates, with some of these showing iron peaks of 22 times that of baseline height (Fig. 3C).

All indications show that the fractionation procedure was effective in making meaningful separations for all samples from the Winisk, Attawapiskat and Moose Rivers. The comparative study employing fractionated Severn River samples indicates that the procedure for assessing the integrity of the colloidal fraction was appropriate. Contamination of the aqueous fractions by particulates of anomalously great size was negligible for the major study. Documenting the lack of iron-rich particulates in the overlap range between colloids and suspended sediment particles facilitates the interpretation of the major study.

Characterization of the Dominant Colloids

Several distinctive types of colloidal "particulates", or colloids, could be characterized according to four standard





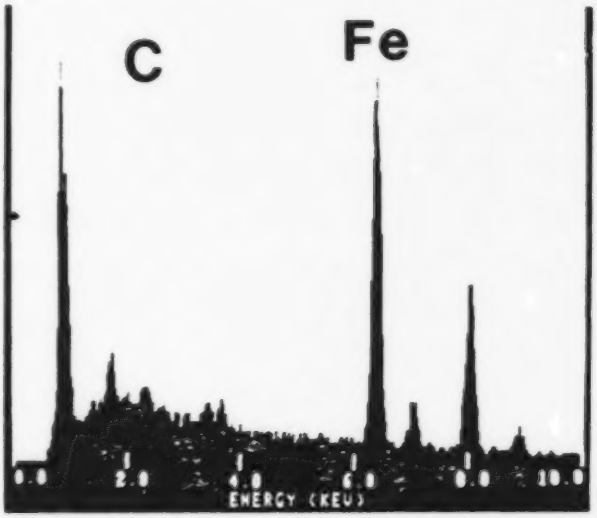


Fig. 3. Representative spectra of colloids and colloid aggregates, showing the K_{α} peak for iron centred around 6.40 keV. Note that the two large peaks centred around 0.93 keV and 8.04 keV are copper peaks generated by the copper grid. All spectra are at FS 1250.

Fig. 3A. Spectrum of a densely packed aggregate of small colloids (including 15-60 nm spheroids) from the Moose River.

Fig. 3B. Spectrum of a loosely packed aggregate of small colloids comparable in irradiated volume to that of Fig. 3A.

Fig. 3C. Spectrum of an angular colloid whose least diameter, 0.35 μm, is in the range of overlap between colloids and conventionally-defined particles. This particulate was taken from the Severn River at a time of great iron enrichment of the colloidal fraction.

morphological parameters (size, shape, manner of aggregation and electron-opacity after application of counterstains). Photomicrographs of the four most common colloids are shown in Fig. 4. The choice of cytological/chemical preparation for the ultrastructural analyses permits a comparison with colloids currently being categorized in a newly evolving ultrastructural literature on aquatic colloids (Burnison and Leppard, 1983; Leppard et al., 1986a).

The dominant colloid types had least diameters near the lower limit of the size range for colloids. Particulates larger than 60 nm (0.060 μm) were infrequent to rare. The high resolution analyses of the shapes and sizes of particulates in the colloidal fraction covered most of the colloidal size range, with practical technical limits being set by the grain structure of the sections (2.5 to 3.0 nm) and by the pore structure of the POC-DOC cutoff filter used in the initial fractionation step (ca. 650 nm). For all colloidal pellets derived by the scheme of Fig. 2, 90-95% of the area covered by particulates on the TEM viewing screen was occupied by particulates smaller than 60 nm. In general, such small colloids were present in numbers two orders of magnitude greater than colloids in the size range of 60-650 nm. Thus 9% of the range accounted for as much as ca. 95% of the pellet and more than 99% of the total particulates.

All colloidal pellets revealed an absence of anomalously large particulates (>> 650 nm) and a near absence of particulates in the range of 100-650 nm. Analyses of filters bearing the suspended sediment fraction were in harmony with the observations on pellets. This means that the fractionation procedure was not producing artifactual particulates in the overlap range between large colloids and conventionally-defined particles.

One type of colloid was dominant in all samples. It was an electron-opaque spheroid of 15-60 nm diameter which aggregated in distinctive linear arrays (Fig. 4A). Sometimes the array was moniliform (Attawapiskat, fall, 1984), sometimes it was a mixture of moniliform and tightly packed arrays (Moose, spring, 1984). Most arrays showed no evidence of a linking structure (as in Fig. 4A -

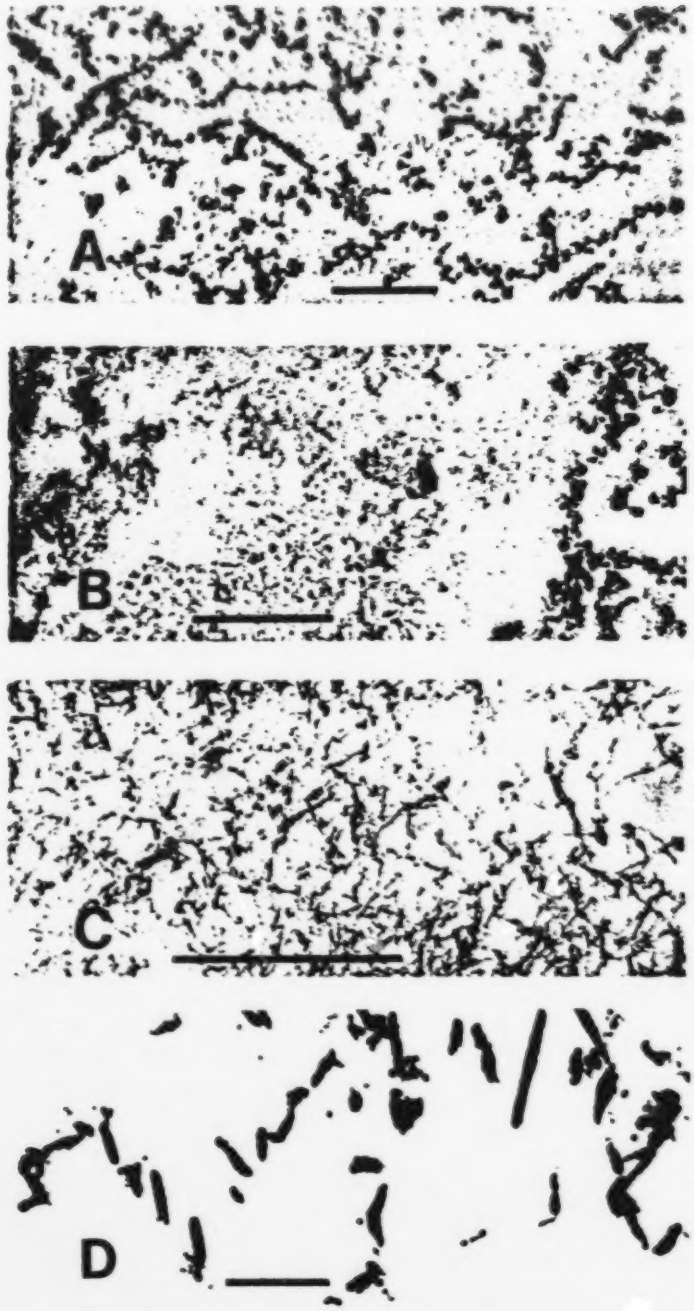


Fig. 4. The most common types of colloids. The bar = 0.45 μm.

Fig. 4A. Electron-opaque spheroids of 15-60 nm aggregated in linear array.

Fig. 4B. Electron-transparent spherules of 3 nm aggregated into spherule clusters, which in turn are aggregated into a porous sponge-like network.

Fig. 4C. Fibrils aggregated into a meshwork.

Fig. 4D. Electron-opaque oblongs, whose least diameter can range from 45-100 nm.

Attawapiskat, spring, 1984) but a small proportion of the arrays in many samples revealed fibrils as linking structures. Of these latter arrays, the fibril was sometimes sharply revealed along its length; sometimes, however, it was fused with the spheroids, with no demarcation of the fibril-spheroid attachment sites. Spheroids were present in colloid aggregates producing an iron peak of the type shown in Fig. 3A.

The most dominant colloid in a numerical sense was an electron-transparent spherule of 3 nm diameter (Fig. 4B - Winisk, spring, 1984). Most of these were aggregated into clusters which in turn were aggregated into a porous sponge-like network. The sponge-like networks were interwoven often with arrays of the 15-60 nm spheroids (Figs. 4A and 4B). In all characteristics examined in this study, the spherules were identical to the spherules of lacustrine pedogenic fulvic acids described by Leppard et al. (1986a).

Other major colloid types included fibrils of moderate electron-opacity (Fig. 4C) and oblong colloids of great electron-opacity (Fig. 4D). Unlike the spheroids and spherules, fibrils and oblongs varied greatly in relative abundance. The fibril contribution to a colloidal pellet varied from negligible (Winisk, spring, 1984) to common, with the atypical sample from the Severn River revealing fibrils to be a dominant component. No pattern to the relative abundance of fibrils could be ascertained. Most were extremely fine (diameter of ca. 3 nm) and there was little evidence of strong aggregation, the exceptions being fibril-spheroid aggregates and occasional meshworks of fibrils (Fig. 4C). In many samples, fibrils of extreme coarseness and variable diameter could be detected. Such extremely coarse fibrils were documented earlier as a minor component of lake water (Massalski and Leppard, 1979 - their Fig. 14) and their existence suggests a "hybridization" of fibrils and spheroids. Some images reveal spheroids connected by fibrils, some reveal fibrils which have an alternation of a thick clumped portion with a fine ribbon-like portion, and some suggest that there is a continuum of types. The

oblongs also presented images suggesting a continuum of types. The oblongs making up a minor component of the colloidal pellet from the Winisk River of spring, 1984 (Fig. 4D) resemble in gross features some linear tightly-packed aggregates of spheroids in the colloidal pellet of the Moose River of spring (1984). The diameters of oblongs and spheroids overlap in the range of 45 to 60 nm and, although the diameter of an oblong can reach 100 nm, most are closer to 60 nm than to 100 nm. Aggregates of electron-opaque oblongs did not yield an iron peak with energy-dispersive spectroscopy but such aggregates were always disperse aggregates, as shown in Fig. 4D; by comparison, the electron-opaque spheroids which produced the type of iron peak shown in Fig. 3A did so when they were part of a large densely-packed clump.

A distinctive electron-opaque globule was found rarely in colloidal pellets from the Moose River. It was too rare to permit establishing a range of sizes for it but it was five times greater in diameter than the typical spheroid (ca. 150 nm compared to ca. 30 nm). Although it made a negligible contribution to colloidal pellets in this study, it is of interest to record it because it is abundant at certain times in surface waters and is known to be enriched in iron and phosphorus compounds (Leppard et al., 1986b).

The Distribution of Organic Carbon and Iron in the Water Fractions

The mass of colloidal organic carbon in the conventionally-defined DOC was similar to the mass of organic carbon in the conventionally-defined POC. The concentration of DOC, as measured in the aqueous fraction, ranged from 10.3 to 18.2 mg/L in the 9 principal samples. The colloidal fraction, however, represented only a small portion of the non-particulate organic carbon, with the concentrations ranging from 0.2 to 0.8 mg/L. Selected results are given for each river in Table 1.

TABLE 1. The distribution of organic carbon and iron in water fractions taken from the Winisk, Attawapiskat and Moose Rivers.

	Winisk Spring 1984	Attawapiskat Fall 1984	Moose Winter 1985
THE COLLOID FRACTION			
Carbon content in mg/L	0.8	0.4	0.4
Fe content in µg/L	12	17	41
Carbon content as fraction of conventional DOC	7.2%	3.4%	2.7%
Fe content as fraction of conventional dissolved Fe	41%	52%	32%
Ratio of carbon to Fe	67	24	10
CHEMICAL DATA ON THE NATURE OF THE SEPARATIONS			
Carbon (mg/L)in			
suspended sediment fraction	0.53	0.36	0.51
aqueous fraction	10.8	11.3	14.3
dissolved fraction	10.2	11.3	14.5
colloidal fraction	0.8	0.4	0.4
Fe (µg/L) in			
raw water	130	79	330
aqueous fraction	40	27	140
dissolved fraction	17	16	88
colloidal fraction	12	17	41
RELATIVE IMPORTANCE OF THE ORGANIC COLLOIDS			
Ratio of total organic carbon to colloidal organic carbon	14	29	37
Ratio of total organic carbon to conventional POC	21	33	29
Ratio of colloidal organic carbon to conventional POC	1.5	1.1	0.8

A summing of the colloidal and dissolved fractions, for both organic carbon and iron content, showed good agreement with the aqueous fraction determinations in seven of the nine sample sets. Based on these seven best sets, the mean non-particulate and colloidal organic carbon contents were 13.3±2.5 and 0.45±0.21 mg/L respectively. Although the colloidal fraction only accounted for 3.6±2.1% of the non-particulate organic carbon, it contained 40±7% of the non-particulate iron. On a mass basis (in terms of organic carbon), the relative iron concentration factor of the colloidal fraction in comparison to the dissolved fraction was 18:1. In view of the facts that the colloids described here were discrete sedimenting entities capable of aggregation and that the iron present in the dissolved fraction behaved as a solute, it becomes interesting to calculate the relative iron concentration factor of the colloidal fraction on a volume basis. The relative iron concentration factor of the colloids, when compared in this way to the dissolved fraction, was on the order of 10^6:1.

DISCUSSION

The information presented here for riverine colloids of the Hudson Bay Lowland shows that they are quantitatively-significant materials and that the conventionally-defined dissolved fraction (aqueous fraction) is a mixture of two different kinds of materials, colloids and solutes, whose properties form a continuum. The principal conclusion is that colloidal phenomena must be considered in ascertaining the mechanisms of iron dispersion in the Winisk, Attawapiskat and Moose Rivers. To this end, the advantages and pitfalls of applying TEM techniques (to analyses of aquatic colloids) have been delineated in the literature and the principal artifact problems can now be investigated systematically (Leppard, 1985).

The new results on riverine colloids are not unexpected in the light of a growing literature on aquatic colloids. However, the specific findings do represent a discrete extension of earlier works which demonstrated that riverine colloids were quantitatively important without reference to a physical characterization of the colloidal fraction.

The large amount of colloidal iron in the aqueous fraction is noteworthy when coupled with the knowledge that colloids are readily subject to aggregation (Vold and Vold, 1964). This means that, potentially, a colloidal carrier of bioavailable iron could very well appear as a solute in one laboratory and as a conventionally-defined particle in another, depending on trivial differences in sample handling and/or storage. The use of a three fraction approach can produce data giving an assessment of such an artifact. In related researches on colloids, we have observed colloid-to-particle transitions resulting from manipulations as gentle as freeze-drying and the concentrating of organic-rich fractions above a level of 200 mg/L (Leppard et al., 1986a).

The use of a three fraction approach is not a new idea but it is an approach which has met considerable resistance because of associated problems such as great increases in cost, time and complexity. In fact, water quality studies have been conducted for five decades using fractionation techniques which ignored the dual nature of DOC and other operationally-defined dissolved fractions. As water managers have generated a need to understand better the mechanisms of heavy metal dispersion, however, this error in approach to water analyses has been stressed with increasing vigor (Breger, 1970; Sharp, 1973; Florence and Batley, 1980; Leppard, 1983). Indeed, Burnison and Leppard (1983) have demonstrated that the colloid fraction of a surface water can account for as much as 33% of the conventionally-defined DOC and the relatively small colloid fractions reported here account for a large portion (sometimes more than 50%) of what is operationally-defined as "dissolved iron". The need to

consider colloids separately from solutes in interpreting metal dispersion data is further emphasized by research on colloidal organic coatings (Neihof and Loeb, 1974; Hunter and Liss, 1979; Hunter, 1980; Leppard, 1984b), colloidal iron coatings (Gibbs, 1973; Boyle et al., 1977) and scattered but significant researches on colloidal associations between iron and organic carbon in river waters (Moore et al., 1979; Florence and Batley, 1980). The research presented here contributes to the central theme of the above-mentioned researches, namely that a three fraction approach yields an opportunity for improved interpretation of metal dispersion data. While this approach requires too many resources to be used on a routine basis, it could be advantageous at certain sites where colloidal phenomena are suspected of generating misleading data. Clearly, the value of producing data collections amenable to realistic interpretation will sometimes offset the accompanying increases in resource needs.

Other scenarios can be presented in support of considering colloidal phenomena. Many aquatic organisms, particularly phytoplankton and epilithic microbes, bear a layer of fibrillar slime on their surface, a layer which increases greatly the interaction surface between cell and aquatic environment. From the riverine analyses reported here, one may speculate that the capture of an iron-rich colloid by a fibrillar slime layer might be the nutritional equivalent of an interaction of that slime layer with iron-containing water having a volume of a million-fold that of the colloid. If such a means of iron nutrition is important in aquatic ecosystems, and there is no reason to believe it is not, then any advances in understanding it and making practical use of the knowledge will rest on analyses of colloidal fractions.

The preparation of all fractions for ultrastructural analyses was done so as to allow for a comparison between riverine particulates and biologically-derived particulates illustrated in the literature on ultrastructure. The literature basis for the formulation of the fixatives is found in Leppard et al. (1977) and comparative studies

relating our method of preparation to other methods, including freeze-etching and acetone fixation, can be found in Burnison and Leppard (1983) and in Leppard et al. (1986a). One can make the following generalizations about the colloids described herein. Fibrils appear as fibrils independently of the technique used to visualize them, although different techniques reveal differences in detail. Spherules of 3 nm diameter have appeared as such in several different laboratories using diverse preparatory techniques and they have been described also in the literature on fulvic acids (for a review see Leppard et al., 1986a). When aggregation of fibrils occurs as a result of fibril interactions with substances used in the TEM preparatory treatments of biologists, the individual fibrils can be recognized as such within an aggregate. However, the same phenomenon is not always true for the 3 nm spherules. Some such spherules identified in the literature have a capacity to aggregate so as to form spheroids which display an increased electron-opacity and no internal differentiation. The spheroids derived in this way (Leppard et al., 1986a) closely resemble the 15-60 nm spheroids illustrated in Fig. 4A. This feature, suggestive of transitions between one type of particulate and another, and three other features make the spheroids a prime subject of interest for future riverine studies. The three other spheroid features are: their abundance; the measurable iron content associated with some of their aggregates; and their tendency to form much larger entities, such as linear arrays.

Future studies should concentrate on the dynamics of spheroid-iron interactions and physicochemical factors which affect spheroid formation and aggregation. Also of interest is the surprising fact that almost all of the colloids taken from the Winisk, Attawapiskat and Moose Rivers had least diameters near the lower limit of the size range for colloids, a fact revealed by no previous riverine studies.

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REFERENCES

Boyle, E.A., J.M. Edmond and E.R. Sholkovitz. 1977. The mechanism of iron removal in estuaries. Geochim. Cosmochim. Acta 41:1313-1324.

Breger, I.A. 1970. What you don't know can hurt you: organic colloids and natural waters, p. 563-574. In D.W. Hood (ed.) Organic matter in natural waters. Institute of Marine Science, Occasional Publ. 1, College, Alaska.

Buffle, J. 1984. Natural organic matter and metal-organic interactions in aquatic systems, ch. 6. In H. Sigel (ed.) Metal ions in biological systems, volume 18, circulation of metals in the environment. Marcel Dekker, New York.

Burnison, B.K. and G.G. Leppard. 1983. Isolation of colloidal fibrils from lake water by physical separation techniques. Can. J. Fish. Aquat. Sci. 40:373-381.

Chandler, J.A. 1977. X-ray microanalysis in the electron microscope. Elsevier/North-Holland Biomedical Press, Amsterdam.

Eisenreich, S.J., M.R. Hoffmann, D. Rastetter, E. Yost and W.J. Maier. 1980. Metal transport phases in the upper Mississippi River, p. 135-176. In M.C. Kavanaugh and J.O. Leckie (eds.) Particulates in water - characterization, fate, effects and removal. American Chemical Society, Washington, D.C.

Florence, T.M. and G.E. Batley. 1980. Chemical speciation in natural waters. CRC Crit. Rev. Anal. Chem. 9:219-296.

Gibbs, R.J. 1973. Mechanisms of trace metal transport in rivers. Science. 180:71-73.

Hunter, K.A. 1980. Microelectrophoretic properties of natural surface-active organic matter in coastal seawater. Limnol. Oceanogr. 25:807-822.

Hunter, K.A. and P.S. Liss. 1979. The surface charge of suspended particles in estuarine and coastal waters. Nature 282:823-827.

Hutton, C.L.A. and W.A. Black. 1975. Ontario Arctic watershed map folio no. 2. Lands Directorate, Environment Canada, Ottawa, Ontario.

Kerndorff, H. and M. Schnitzer. 1980. Sorption of metals on humic acid. Geochim. Cosmochim. Acta 44:1701-1708.

Laxen, D.P.H. and I.M. Chandler. 1983. Size distribution of iron and manganese species in freshwaters. Geochim. Cosmochim. Acta 47:731-741.

Leppard, G.G. (ed.) 1983. Trace element speciation in surface waters and its ecological implications. Plenum Publishing Corporation, New York.

Leppard, G.G. 1984a. Relationships between fibrils, colloids, chemical speciation, and the bioavailability of trace heavy metals in surface waters - a review. National Water Research Institute Contribution No. 84-45, Burlington, Ontario, Canada.

Leppard, G.G. 1984b. Organic coatings on suspended particles in lake water. Arch. Hydrobiol. 102:265-269.

Leppard, G.G. 1985. Transmission electron microscopy applied to water fractionation studies - a new look at DOC. Wat. Pollut. Res. J. Can. 20(2):100-110.

Leppard, G.G., J. Buffle and R. Baudat. 1986a. A description of the aggregation properties of aquatic pedogenic fulvic acids - combining physico-chemical data and microscopical observations. Water Res. 20:185-196.

Leppard, G.G., J. Buffle and R. De Vitre. 1986b (in preparation). The ultrastructural and physical characteristics of a distinctive colloidal iron particulate isolated from a small eutrophic lake.

Leppard, G.G., A. Massalski and D.R.S. Lean. 1977. Electron-opaque microscopic fibrils in lakes: their demonstration, their biological derivation and their potential significance in the redistribution of cations. Protoplasma 92:289-309.

Mantoura, R.F.C. 1981. Organo-metallic interactions in natural waters, p. 179-223. In E.K. Duursma and R. Dawson (eds.) Marine organic chemistry - evolution, composition, interactions and chemistry of organic matter in seawater. Elsevier Scientific Publishing Company, Amsterdam.

Massalski, A. and G.G. Leppard. 1979. Survey of some Canadian lakes for the presence of ultrastructurally discrete particles in the colloidal size range. J. Fish. Res. Board Can. 36:906-921.

McCrea, R.C. and J.C. Merriman. 1981. Water quality in the Moose River - a pilot study, 1977-1798. Report Series No. 70, Inland Waters Directorate, Ontario Region, Water Quality Branch, Burlington, Ontario.

McCrea, R.C. and J.D. Fischer. 1986. Heavy metal and organochlorine contaminants in the five major Ontario rivers of the Hudson Bay Lowland. Wat. Pollut. Res. J. Can. 21(2):225-234.

Moore, R.M., J.D. Burton, P.J. LeB. Williams and M.L. Young. 1979. The behaviour of dissolved organic material, iron and manganese in estuarine mixing. Geochim. Cosmochim. Acta 43:919-926.

Neihof, R. and G. Loeb. 1974. Dissolved organic matter in seawater and the electric charge of immersed surfaces. J. Mar. Res. 32:5-12.

Peachey, L.D. 1958. Thin sections-I. a study of section thickness and physical distortion produced during microtomy. J. Biophys. Biochem. Cytol. 4:233-242.

Schnitzer, M. 1981. Reactions of humic substances with metals and minerals in soils. Colloques internationaux du C.N.R.S., pp. 229-234 in No. 303, Migrations organo-minérales dans les sols tempérés. Paris, France.

Sharp, J.H. 1973. Size classes of organic carbon in seawater. Limnol. Oceanogr. 18:441-447.

Sholkovitz, E.R. and D. Copeland. 1980. The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in a river water. Geochim. Cosmochim. Acta 45:181-189.

Sims, R.A., J.L. Riley and J.K. Jeglum. 1979. Vegetation, flora and vegetation ecology of the Hudson Bay Lowland: a literature review and annotated bibliography. Environment Canada, Canadian Forestry Service Rep. O-X-297.

Spurr, A.R. 1969. A low-viscosity epoxy resin embedding medium for electron microscopy. J. Ultrastruct. Res. 26:31-43.

Tipping, E. 1981. The adsorption of aquatic humic substances by iron oxides. Geochim. Cosmochim. Acta 45:191-199.

Tipping, E. and M. Ohnstad. 1984. Colloid stability of iron oxide particles from a freshwater lake. Nature 308:266-268.

Vold, M.J. and R.D. Vold. 1964. Colloid chemistry, the science of large molecules, small particles and surfaces. Reinhold Publ. Corp., New York.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Toronto, Canada.